

PATENT ABSTRACTS OF JAPAN

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(54) NONAQUEOUS ELECTROLYTE BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a nonaqueous electrolyte battery which can improve yield of a battery by restraining degradation of adhesion between graphites themselves or a graphite and a core body through restraint of sliding of basal faces, even when electrode plates are milled by a roller press for upgrading filling density of a negative active material.

SOLUTION: With a nonaqueous electrolyte battery provided with a negative electrode with a negative active material layer formed with a negative active material, as a main constituent, made of graphite (of L_c value of 150\AA or more, and $d_{(002)}$ value of less than 3.38\AA ;) on the surface of a negative electrode core body made of copper foil, a positive electrode equipped with a positive active material layer which can store and release lithium, and a nonaqueous electrolyte, the above graphite is regulated to have a peak intensity ratio $(I_{(002)}/I_{(110)})$ of (002) face to (110) face by powder X-ray diffraction method using a Cu-K α line source at 1,000 or less.

JAPANESE

[JP,2001-283844,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL
FIELD PRIOR ART EFFECT OF THE INVENTION
TECHNICAL PROBLEM MEANS EXAMPLE

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1]A negative electrode in which a negative electrode active material layer which makes a subject negative electrode active material which comprises black lead (Lc value is not less than 150A, and a $d_{(002)}$ value is 3.38A or less) was formed in the surface of a negative-electrode axis which comprises copper foil.

An anode provided with occlusion and a positive active material layer which may be emitted for lithium.

Nonaqueous electrolyte.

It is the nonaqueous electrolyte battery provided with the above, and a peak intensity ratio ($I_{(002)}/I_{(110)}$) of a field and a field (110) by powder X-ray diffractometry (002) for which the above-mentioned black lead used a source of Cu-

K alpha rays is regulated by 1000 or less.

[Claim 2]The nonaqueous electrolyte battery according to claim 1 with which thickness of a negative-electrode axis which comprises said copper foil is regulated by not less than 5 micrometers 10 micrometers or less.

[Claim 3]The nonaqueous electrolyte battery according to claim 1 or 2 with which pack density of negative electrode active material in said negative electrode plate is regulated [cc] in not less than 1.5g/cc 1.8g /or less.

[Claim 4]The nonaqueous electrolyte battery according to claim 1, 2, or 3 which spheroidizes when said negative electrode active material makes high pressure gas blow off with a jet mill.

[Translation done.]

JAPANESE

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the nonaqueous electrolyte battery which has the negative electrode in which the negative electrode active material layer which makes a subject negative electrode active material which comprises black lead was formed in the surface of the negative-electrode axis which comprises copper foil, the anode provided with occlusion and the positive active material layer which may be emitted for lithium, and nonaqueous electrolyte.

[0002]

[Description of the Prior Art] In recent years, while using lithium containing transition metal oxides, such as LiCoO_2 , etc. as positive active material, the nonaqueous electrolyte battery used as negative electrode active material attracts [carbon materials /, such as occlusion, an alloy which may be emitted, an oxide or black lead, and corks,] attention in metal lithium or a lithium ion as a cell in which high-capacity-izing is possible.

[0003] When the material which makes lithium or lithium a subject among the above-mentioned negative electrode active material is used, Lithium of arborescence deposits by charge and discharge (a dendrite occurs), and when a carbon material is used as a negative pole material to there being a possibility of connecting too hastily within a cell, there is an advantage that such a fault is cancelable. Also in it, when black lead is used, service

capacity increases, and early charge and discharge efficiency improves, and there is an advantage that the surface smoothness of potential is secured.

[0004]Here, in producing a negative electrode using the above-mentioned black lead, after mixing a binder etc. with black lead and preparing a slurry first, the negative-electrode axis which comprises copper foil is plastered with this slurry, and this is dried further. The polar plate finally produced as mentioned above in order to raise the pack density of negative electrode active material is rolled with a roller press.

[0005]However, conventional black lead is the shape of a piece of Lynn. With [black lead with a larger peak intensity ratio $I_{(002)}/I_{(110)}$] of the

field by the powder X-ray diffractometry (002) using the source of Cu-K alpha rays, this (002) field, and a vertical (110) field than 1000]. Since the amount of preferred orientation is high, the rate that orientation of the Bay Sal side is carried out to parallel with the plane direction of a polar plate becomes high. As a result, when rolling a polar plate with a roller press, the Bay Sal sides were slippery, the adhesion of black lead or black lead, and an axis fell, and it had the technical problem that the yield of a cell became low.

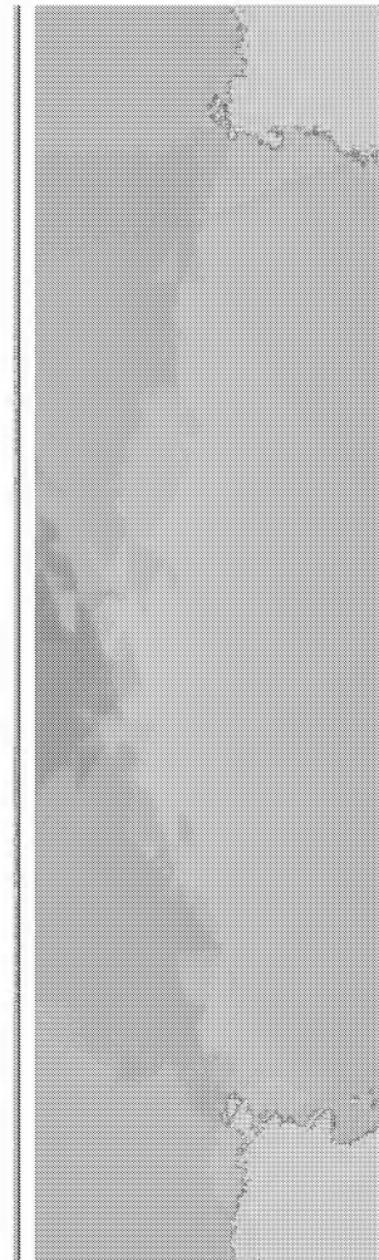
[0006]

[Problem(s) to be Solved by the Invention]Even if it is a case where a polar plate is rolled with a roller press so that this invention may raise the pack density of negative electrode active material in consideration of the above-mentioned conventional technical problem, By controlling that the Bay Sal sides are slippery, it stops that the adhesion of black lead or black lead, and an axis falls, and aims at providing the nonaqueous electrolyte battery which can raise the yield of a cell.

[0007]

[Means for Solving the Problem]To achieve the above objects, among this inventions the invention according to claim 1, A negative electrode in which a negative electrode active material layer which makes a subject negative electrode active material which comprises black lead (Lc value is not less than 150A, and a $d_{(002)}$ value is 3.38A or less) was formed in the surface of a negative-electrode axis which comprises copper foil, It is a nonaqueous electrolyte battery which has an anode provided with occlusion and a positive active material layer which may be emitted for lithium, and nonaqueous electrolyte, A peak intensity ratio $(I_{(002)}/I_{(110)})$ of a field and a field (110) by powder X-ray diffractometry [black lead / above-mentioned] (002) using a source of Cu-K alpha rays is regulated by 1000 or less.

[0008]If a peak intensity ratio $(I_{(002)}/I_{(110)})$ with a field where black lead is vertical to a field by powder X-ray diffractometry (002) which used a source of Cu-K alpha rays, and this (002) field like the above (110) is regulated by 1000 or less, it will become spherical black lead. Therefore, since it can control that the Bay Sal sides are slippery even if it is a case where a polar plate is rolled with a roller press in order to raise pack density of negative electrode active material, it can stop that the adhesion of negative electrode active material falls. As a result, it becomes possible



to raise a yield of a cell by leaps and bounds.

[0009]Thickness of a negative-electrode axis in which the invention according to claim 2 comprises said copper foil in the invention according to claim 1 is regulated by not less than 5 micrometers 10 micrometers or less.

[0010]Thus, regulating thickness of a negative-electrode axis which comprises copper foil, It is because it is necessary to raise pack density of negative electrode active material remarkably so if thickness of a negative-electrode axis exceeds 10 micrometers while a negative-electrode axis may fracture, and a load characteristic will fall and adhesion strength in a negative electrode will moreover also fall, if thickness of a negative-electrode axis is less than 5 micrometers.

[0011]Pack density of negative electrode active material [in / on the invention according to claim 1 or 2 and / in the invention according to claim 3 / said negative electrode plate] is regulated in not less than 1.5g/cc 1.8g/cc or less.

[0012]Thus, regulating pack density of negative electrode active material, It is because a load characteristic will fall and adhesion strength in a negative electrode will fall, if pack density of negative electrode active material exceeds cc in 1.8g /while negative-electrode capacity per unit volume will fall, if pack density of negative electrode active material becomes in less than 1.5g/cc.

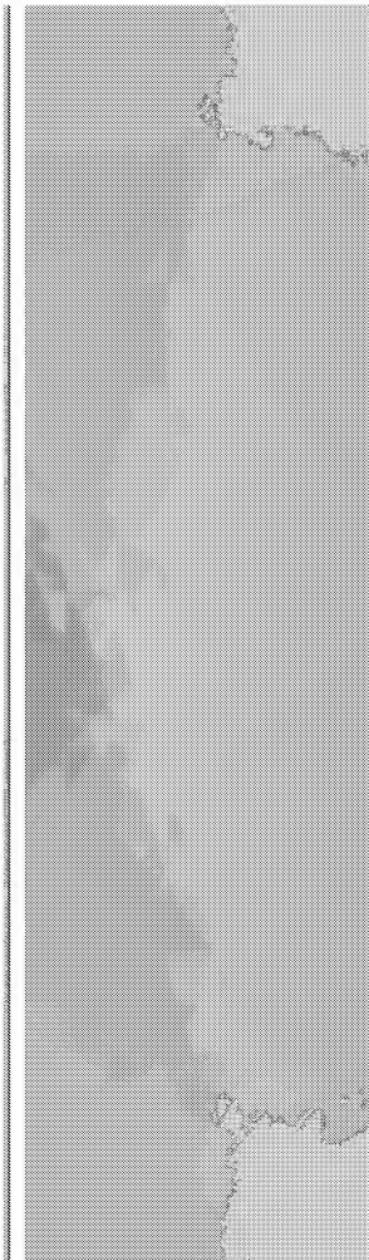
[0013]In the invention according to claim 1, 2, or 3, the invention according to claim 4 spheroidizes, when said negative electrode active material makes high pressure gas blow off with a jet mill.

[0014]With such a manufacturing method, although nodular graphite can be obtained, this invention is not limited to such a method.

[0015]

[Embodiment of the Invention](Production of an anode) First, the LiCoO_2 powder (mean particle diameter: 5 micrometers) as positive active material and the artificial-graphite powder as a conducting agent were mixed at a rate of 9:1 by the weight ratio, and positive electrode mixture was produced. Next, this positive electrode mixture and the N-methyl-2-pyrrolidone (NMP) solution in which the polyvinylidene fluoride as a binder was dissolved 5% of the weight, After having mixed so that a solid content weight ratio might be set to 95:5, and preparing a slurry, this slurry was applied to both sides of the aluminium foil as an anode axis with the doctor blade method (thickness is 100 micrometers of each field). Then, after drying the solvent and compressing even into predetermined thickness with a roller, vacuum drying was carried out at 150 ** for 2 hours, and the anode (pack density of an active material : 3.0g/(cc)) was produced.

(Production of a negative electrode) It is piece of Lynn-like natural graphite first. [The peak intensity ratio of the field and field (110) by the powder X-ray diffractometry (002) using the source of Cu-K alpha rays ($I_{(002)}/I_{(110)}$). (It carries out abbreviated to a peak intensity ratio hereafter) 500, Lc value:780A, $d_{(002)}$ value:3.358A, Mean particle diameter: A peak intensity ratio is nodular graphite of 500 by loading a counter jet mill with



500g 40 micrometer], setting it as pneumatic pressure 4kg/cm² and the diameter phi of a jet nozzle of 5 mm, and operating a counter jet mill for 20 minutes. [Lc value: 780-A, d₍₀₀₂₎ value:3.358A, and mean-particle-diameter:20-micrometer] was produced.

[0016]Next, water was made to distribute the above-mentioned nodular graphite and the dispersion (solid content: 48%) of the styrene butadiene rubber (SBR) as a binder, carboxymethyl cellulose (CMC) which is a thickener was added further, and the slurry was prepared. The weight ratio after negative-electrode desiccation mixed the mixing ratio of the above-mentioned nodular graphite, SBR, and CMC so that it might be set to nodular graphite:SBR:CMC=100:3:2. Then, the above-mentioned slurry was applied to both sides of copper foil (thickness: 8 micrometers) as a negative-electrode axis with the doctor blade method (thickness is 100 micrometers of each field). After drying the solvent and compressing even into predetermined thickness with a roller after an appropriate time, vacuum drying was carried out at 110 ** for 2 hours, and the negative electrode (pack density of an active material : 1.5g/(cc)) was produced. (Preparation of an electrolysis solution) As an electrolysis solution, LiPF₆

used the nonaqueous electrolyte dissolved at a rate of 1M (a mol/liter) for the mixed solvent with which EC (ethylene carbonate) and DEC (diethyl carbonate) were mixed at a rate of 50:50 by the volume ratio.

(Production of a cell) After winding the above-mentioned anode and the negative electrode via the separator which comprises the fine porous membrane made from polypropylene and producing a power generation element, this power generation element was inserted into the cylinder-like-object-with-base-like armor can. Finally, after pouring in the above-mentioned electrolysis solution into an armor can, the cell (AA size, theoretical capacity: 600 mA) of the cylindrical shape was produced by attaching an obturation board to the opening of an armor can.

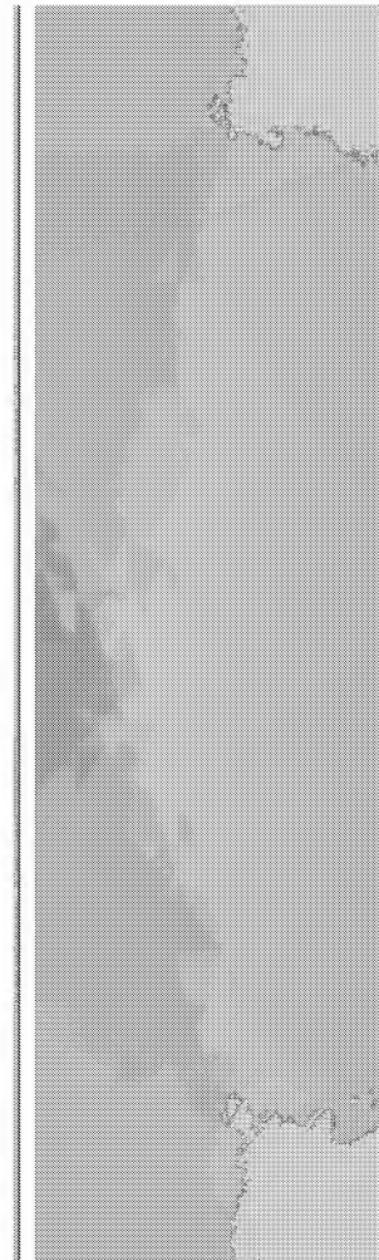
[0017]the above -- although natural graphite was used as black lead as a charge of a start material in the embodiment of the invention, it is also possible for it not to be limited to this and to use an artificial graphite.

[0018]It is possible for it not to be limited to the above-mentioned LiCoO₂, and to use other lithium content metal multiple oxides (as metal,

at least one sort chosen from Co, Mn, nickel, V, and Nb is used) etc. as a positive electrode material.

[0019]Not only the above-mentioned thing as a solvent of an electrolysis solution but ethylene carbonate, Propylene carbonate, butylene carbonate, vinylene carbonate, Cyclopentanone, sulfolane, 3-methyl sulfolane, 2,4-dimethylsulfolane, 3-methyl 1,3-oxazolidine 2-one, gamma-butyrolactone, Dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, Methylpropyl carbonate, butylmethyl carbonate, ethylpropyl carbonate. They may be simple substances, such as butylethyl carbonate, dipropyl carbonate, 1,2-dimethoxyethane, a tetrahydrofuran, 2-methyltetrahydrofuran, 1,3-dioxolane, methyl acetate, and ethyl acetate, or two ingredients, and three component mixtures.

[0020]In addition, as a solute of an electrolysis solution, it may be not only the above-mentioned thing but LiBF₄, LiCF₃SO₃, LiAsF₆, LiN(CF₃SO₂)



2, LiClO₄, etc.

[0021] As a binder, do not limit to the above-mentioned thing and Methyl (meta) acrylate, Ethyl (meta) acrylate, butyl (meta) acrylate, acrylonitrile (meta), Ethylenic unsaturated carboxylic acid, such as ethylenic-unsaturated-carboxylic-acid ester, such as hydroxyethyl (meta) acrylate, or acrylic acid, methacrylic acid, itaconic acid, fumaric acid, and maleic acid, can also be used.

[0022]

[Example](The 1st example)

[Example 1] as Example 1 -- the above -- the cell produced in the method shown in an embodiment of the invention and the similar way was used.

[0023] Thus, the produced cell is hereafter called this invention cell A1.

[Examples 2-4] Pack density of negative electrode active material was respectively set to cc in 1.4g [cc], 1.8g [cc], and 1.9g /, and also the cell was produced like the above-mentioned Example 1.

[0024] Thus, the produced cell is hereafter called this invention cell A2 - A4, respectively.

[Examples 5-8] The peak intensity ratio was set to 300, and also the cell was respectively produced like the above-mentioned Example 1 - Example 4.

[0025] Thus, the produced cell is hereafter called this invention cells A11-A14, respectively.

[Examples 5-8] The peak intensity ratio was set to 1000, and also the cell was respectively produced like the above-mentioned Example 1 - Example 4.

[0026] Thus, the produced cell is hereafter called this invention cells A21-A24, respectively.

[Comparative examples 1-4] The peak intensity ratio was set to 1500, and also the cell was respectively produced like the above-mentioned Example 1 - Example 4.

[0027] Thus, the produced cell is hereafter called the comparison cells X1-X4, respectively.

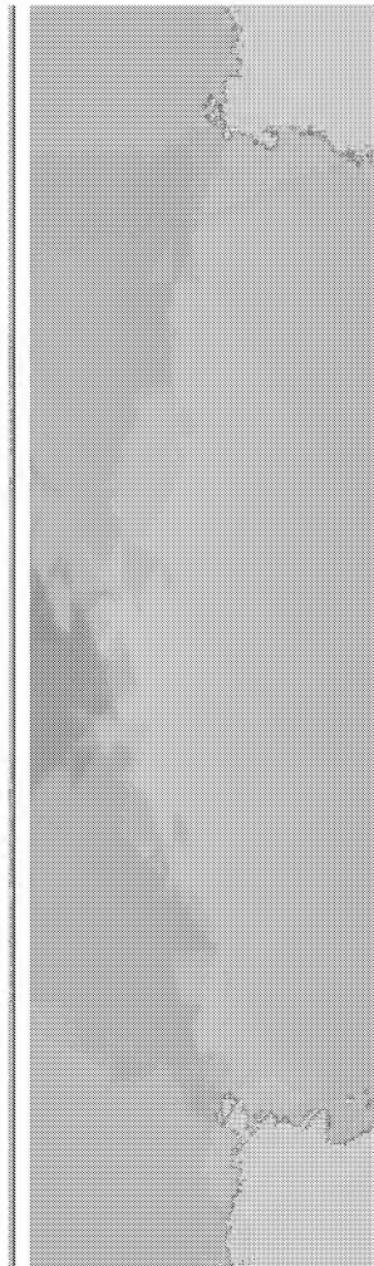
[Comparative examples 5-8] The peak intensity ratio was set to 2000, and also the cell was respectively produced like the above-mentioned Example 1 - Example 4.

[0028] Thus, the produced cell is hereafter called comparison cell X11-X14, respectively.

[Experiment] Since the adhesion strength of the negative electrode was investigated using this invention cell A1 - A4, A11-A14, A21-A24 and the comparison cells X1-X4, X11 - the negative electrode in X14, the result is shown in Table 1. The measuring method of the adhesion strength of a negative electrode sticks the double-sided tape of 1 cm² on each negative electrode, It carries out by investigating load when pulling up perpendicularly to a negative-electrode flat surface, and the pack density of negative electrode active material shows load in case a peak intensity ratio is 300 in cc in 1.4g /as 100% in Table 1.

[0029]

[Table 1]



ピーク強度比	電池の種類	負極活性物質の充填密度	負極の密着強度
300	本発明電池A12	1.4 g/cc	100
	本発明電池A11	1.5 g/cc	100
	本発明電池A13	1.8 g/cc	100
	本発明電池A14	1.9 g/cc	90
500	本発明電池A2	1.4 g/cc	100
	本発明電池A1	1.5 g/cc	100
	本発明電池A3	1.8 g/cc	100
	本発明電池A4	1.9 g/cc	90
1000	本発明電池A22	1.4 g/cc	99
	本発明電池A21	1.5 g/cc	98
	本発明電池A23	1.8 g/cc	97
	本発明電池A24	1.9 g/cc	87
1500	比較電池X2	1.4 g/cc	80
	比較電池X1	1.5 g/cc	70
	比較電池X3	1.8 g/cc	68
	比較電池X4	1.9 g/cc	58
2000	比較電池X12	1.4 g/cc	70
	比較電池X11	1.5 g/cc	60
	比較電池X13	1.8 g/cc	58
	比較電池X14	1.9 g/cc	48

[0030]Compared with the comparison cells X1-X4, X11 - X14, it is admitted this invention cell A1 - A4, A11-A14, A21 - A24 that the adhesion strength of a negative electrode is large so that clearly from the above-mentioned table 1. Therefore, the field of the adhesion strength of a negative electrode shows that it is desirable for a peak intensity ratio to use 1000 or less nodular graphite as negative electrode active material.

[0031]it is admitted that this invention cell A1 - A3, A11-A13, A21 - A23 are boiled and compared with this invention cell A4, A14, and A24, and the adhesion strength of a negative electrode is still larger. The thing [that the negative-electrode capacity per unit volume will fall if the pack density of negative electrode active material becomes in less than 1.5g/cc, although not shown in the above-mentioned table 1 on the other hand] was accepted. Therefore, in order to prevent the fall of negative-electrode capacity, raising the adhesion strength of a negative electrode further, it turns out that it is desirable for a peak intensity ratio to regulate [cc] the pack density of negative electrode active material in 1.5g/cc - 1.8g / moreover, using 1000 or less nodular graphite as negative electrode active material.

[0032](The 2nd example)

[Examples 1-6] As shown in the following table 2, the thickness of copper foil and the pack density of negative electrode active material which are negative-electrode axes were changed, and also the cell was produced like Example 1 of the 1st example of the above. The thickness of each negative electrode is the same as the negative electrode shown in Example 1 of the 1st example of the above.

[0033]Thus, the produced cell is hereafter called this invention cell B1 - B6, respectively.

[Experiment] Since the load characteristic of this invention cell A1 shown in said 1st example and the above-mentioned this invention cell B1 - B6 was investigated, the result is shown in Table 2. The rate of the service capacity (temperature: 25 ***) in the current [as opposed to / a load characteristic performs charge and discharge on condition of the following, and / the service capacity (temperature: 25 ***) in the current 1C (600 mA)] 2C (1200 mA) It is shown by [service capacity x100 (%) in the service capacity / current 2C in the current 1C].

[0034]Charge condition: Charge after charging until cell voltage is set to 4.1V with the current 1C until current falls by 10 mA by the constant potential charge of 4.1V.

[0035]Discharging condition: Discharge until cell voltage is set to 2.75V by the current 1C or 2C.

[0036]

[Table 2]

電池の種類	銅箔の厚み	負極活性物質の充填密度	負荷特性
本発明電池 B 1	3 μ m	1. 4 g / c c	負極作製できず
本発明電池 B 2	5 μ m	1. 5 g / c c	1 0 0
本発明電池 A 1	8 μ m	1. 5 g / c c	1 0 0
本発明電池 B 3	10 μ m	1. 5 g / c c	1 0 0
本発明電池 B 4	12 μ m	1. 6 g / c c	9 0
本発明電池 B 5	15 μ m	1. 7 g / c c	6 5
本発明電池 B 6	20 μ m	1. 8 g / c c	5 0

[0037]The thickness of copper foil which is a negative-electrode axis in this invention cell B4 over 10 micrometers - B6 so that clearly from the above-mentioned table 2. Since it is necessary to enlarge pack density of negative electrode active material, a load characteristic falls and there is a problem that a negative-electrode axis has too thin the thickness of copper foil by this invention cell B1 below 5 micrometers, and a negative electrode fractures. On the other hand, there is no problem that a negative electrode fractures and, moreover, it excels in a load characteristic this invention cell A1, B-2, and B3.

[0038]Therefore, in order to aim at improvement in a load characteristic, preventing the fracture of a negative electrode, it is desirable to regulate the thickness of copper foil which is a negative-electrode axis to 5-10 micrometers.

[0039]

[Effect of the Invention]As explained above, even if it is a case where a polar plate is rolled with a roller press in order to raise the pack density of negative electrode active material, by this invention, it controls that the Bay Sal sides are slippery.

Therefore, it stops that the adhesion of black lead or black lead, and an axis falls, and the outstanding effect that the yield of a cell can be raised is done so.

[Translation done.]

